PATENT ABSTRACTS OF JAPAN

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(54) MANUFACTURE OF SUPPORT FOR LITHOGRAPHIC PLATE

(57)Abstract:
PROBLEM TO BE SOLVED: To further improve the properties of difficulty to interlock by further enhancing water retention characteristics beyond the current level in a method for manufacturing a support for lithographic plate.
SOLUTION: This method for manufacturing a support for a lithographic plate is to repeatedly perform an electrolytic surface roughening process to an aluminum support in an acid electrolytic solution, introducing an aluminum etching process between the steps of the former. In this method, the average diameter of a pit formed by a first electrolytic surface roughening step is set to 2-25ì m and the average diameter of the pit formed by a following electrolytic roughening step is set to 1/2 or less or 1/30 or more of the average diameter of the pit formed by the preceding electrolytic surface roughening step. In this case, the acid electrolytic solution for the electrolytic surface roughening process is an aqueous solution composed mainly of nitric acid. Further, the variation of the pit diameter can be controlled by differentiating the electrolytic solution temperature, concentration, current density, power supply frequency, power supply waveform and ratio of forward/reverse current times of the following step from those of the preceding step.

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CLAIMS

[Claim(s)]
[Claim 1] In the manufacture method of the base material for the printing versions which performs electrolysis split-face-ized processing in the middle repeatedly on both sides of etching processing of aluminum for an aluminum plate in the acid electrolytic solution The manufacture method of the base material for the lithography versions characterized by making the diameter of an electrolysis split-face-ized average pit of a back process into 1/2 or less [of the diameter of an electrolysis split-face-ized average pit of a last process], and 1/30 or more, using the diameter of an electrolysis split-face-ized average pit of the 1st process as 2 micrometers - 25 micrometers.
[Claim 2] The manufacture method of the base material for the monotonous printing versions according to claim 1 characterized by the aforementioned acid electrolytic solution for electrolysis split-face-ized processing being the solution which makes a nitric acid a subject.
[Claim 3] Before the formation of an electrolysis split face of the 1st process, it is the formation of a mechanical split face, 0.1-30/m2 to an aluminum plate. Chemical etching processing is performed. It is 50 - 600 c/dm2 in the electrolytic solution which includes electrolysis split-face-ization of this 1st process for a 10-50-degree C nitric acid. It carries out. Before the formation of an electrolysis split face of a back process, it is 0.1 - 20 g/m2. Chemical etching processing is performed. It is 10 - 200 c/dm2 in the electrolytic solution which includes electrolysis split-face-ization of this back process for a 35-80-degree C nitric acid. It carries out. after the formation of an electrolysis split face of a back process Chemical etching processing of 0.01 - 2 g/m2, The manufacture method of the base material for the monotonous printing versions according to claim 1 characterized by performing anodizing.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the manufacture method of the base material for the printing versions which consists of a split-face-ized aluminum plate of being suitable for especially offset plates, about the manufacture method of the base material for the printing versions. Moreover, this invention relates also to the manufacture method of the base material for the lithography versions which was excellent in the difficulty of being involved, and the difficulty of becoming dirty, and was excellent also in print durability.
[0002]
[Description of the Prior Art] As the base material for the printing versions, especially a base material for offset plates, the aluminum plate (an aluminium alloy board is included) is used. In order to use an aluminum plate as a plate for offset printing (base material) generally, it is required to have a moderate adhesive property and moderate water retention with sensitization material. For that, you have to split-face-ize the front face of an aluminum plate so that it may have a uniform and precise grain. Since it has remarkable influence on the printing performance and print durability of a plate when this split-face-ized processing actually performs offset printing after platemaking, the quality serves as an important element on plate manufacture. Generally as a split-face-ized method of the aluminum base material for the printing versions, the alternating-current-electrolysis etching method is adopted, and special police box wave current, such as sine-wave-alternating-current current ordinary as current and a square wave, is used. And by making suitable electrodes, such as a graphite, into a counter electrode, split-face-ized processing of an aluminum plate is performed and it is usually carried out by alternating current by one processing. Then, on the whole, the thinness of the pit obtained was shallow, and was a thing inferior to print durability ability. For this reason, many methods are proposed so that an aluminum plate suitable as a base material for the printing versions which has the grain in which the pit where the depth is deep exists uniformly and precisely as compared with the diameter may be obtained. As the method, the combination (JP,56-29699,A) of the ratio (JP,54-65607,A) of quantity of electricity at the time of the anode plate at the time of the formation of the electrolysis split face using the alternating current and cathode, a power supply wave (JP,55-25381,A), and the amount of energization per unit area etc. is known. Moreover, JP,57-16918,B is known as a method which combined the mechanical split-face-ized method and the electrolysis split-face-ized method. Furthermore, the manufacture method (JP,7-29507,B) of the aluminum base material for the printing versions characterized by performing electrolysis split-face-ized processing in the middle repeatedly on both sides of etching processing of aluminum for an aluminum base material in the acid electrolytic solution again is indicated.
[0003]
[Problem(s) to be Solved by the Invention] However, although the performance these methods excelled [performance] in a dirt performance and water resistance was shown, it was inadequate in raising a performance (dirt of the non-picture section of the half-tone-dot section) in the difficulty of being involved by raising water retention.
[0004] The purpose of this invention is by raising water retention further from before to offer the

manufacture method of the base material for the printing versions which can raise a performance much more in the difficulty of being involved. Other purposes of this invention are to offer the manufacture method of the base material for the lithography versions which was excellent in the difficulty of becoming dirty with improvement in a performance in the above difficulty of being involved, and was excellent also in print durability.

[0005]

[Means for Solving the Problem] this invention person etc. performs variously dissolution processing of the edge portion of the pit generated by electrification split-face-ized processing as a result of research. By producing the diameter of an electrolysis split-face-ized average pit of 1/2 or less back process of the diameter of a last process electrolysis split-face-ized average pit using an alternating current wave in the electrolytic solution which pulls and continues and contains a nitric acid again, after making an edge front face gently-sloping It discovered that water retention was raised and a performance might be raised much more in the difficulty of being involved, and resulted in this invention. Namely, the above-mentioned purpose of this invention is set to the manufacture method of the base material for the printing versions which performs electrolysis split-face-ized processing in the middle repeatedly on both sides of etching processing of aluminum for an aluminum base material in the acid electrolytic solution. It is attained by the manufacture method of the base material for the lithography versions characterized by making the diameter of an electrolysis split-face-ized average pit of a back process into 1/2 or less [of the diameter of an electrolysis split-face-ized average pit of a last process], and 1/30 or more, using the diameter of the 1st process electrolysis split-face-ized average pit as 2 micrometers - 25 micrometers. In the manufacture method of the above-mentioned base material for the lithography versions furthermore, as a desirable mode Before the formation of an electrolysis split face of the 1st process of the above, to an aluminum plate, the formation of a mechanical split face, 0.1-30/m2 Chemical etching processing is performed. electrolysis split-face-ization of this 1st process It is 50 - 600 c/dm2 in the electrolytic solution containing a 10-50-degree C nitric acid. It carries out. Before the formation of an electrolysis split face of a back process, it is 0.1 - 20 g/m2. Chemical etching processing is performed. It is 10 - 200 c/dm2 in the electrolytic solution which includes electrolysis split-face-ization of this back process for a 35-80-degree C nitric acid. It carries out. after the formation of an electrolysis split face of a back process Chemical etching processing of 0.01 - 2 g/m2, It is the manufacture method of the base material for the monotonous printing versions according to claim 1 characterized by performing anodizing.

[0006]

[Embodiments of the Invention] As for the acid electrolytic solution for electrolysis split-face-ized processing, in this invention, it is desirable that it is the solution which makes a nitric acid a subject. Forming an electrolysis split face in the acid electrolytic solution in this invention is passing alternating current in the electrolytic solution containing a nitric acid between an aluminum plate and the electrode which counters this, and it performs electrolysis split-face-ized processing. In this case, it is the solution which contains a nitric acid in 5-400g/l. as the electrolytic solution, and it is desirable that it is in the range of current density 1 - 200 A/dm2, and 30-80 degrees of solution temperature C. As for the electrolysis split-face-ized processing time, it is desirable that it is in the range for 5 - 90 seconds. Moreover, even if the current wave form used by electrolysis split-face-ized processing is not limited to an alternating current and uses a direct current, it is possible. The alternating current wave used by this invention is current of the wave which is made to change the polarity of positive/negative by turns and is acquired, and the voltage-waveform view is illustrated to drawing 1 and drawing 2 . In drawing 2 , although that to which (a) carried out the sine wave by the sine wave, and (b) carried out phase angle control by the thyristor, and (c) show the power supply wave of a square wave, although the alternating current wave of this invention was described above, they do not restrict it to a power supply wave. Moreover, as the electrolytic solution used for electrolysis split-face-ized processing in this invention, it is not limited to a nitric acid, and the mixed liquor of a hydrochloric acid or a hydrochloric acid, a nitric acid and a nitric acid, and a sulfuric acid may be used. You may use mixed liquor with a phosphoric acid or a phosphoric acid, a sulfuric acid, or

other acids instead of a sulfuric acid in that case.
[0007] In this invention, the thing of the pit which generated the etching processing inserted in the middle of electrolysis split-face-ized processing by electrolysis split-face-ized processing of the preceding paragraph for which especially an edge portion is dissolved is said. As processing conditions, each technique of well-known etching processing can use etching of the aluminum by being immersed, electrolytic polishing in the inside of being immersed [caustic alkali of sodium], a phosphoric acid, or the sulfuric-acid electrolytic solution, etc. for a long time [to an elevated-temperature sulfuric-acid solution]. However, it is necessary to consider before and behind it so that the etching reagent after electrolysis split-face-ized processing and electrolysis split-face-ized processing liquid may not be mixed.
[0008] Although electrolysis split-face-ized processing may be repeatedly performed how many times in this invention, it is desirable on the simplification of a process to consider as 1 time the back once a front on both sides of the etching processing in middle. Repeating electrolysis split-face-ized processing on both sides of etching processing in this invention It is performing electrolysis split-face-ization which passes alternating current between an aluminum plate and the electrode which counters this in the electrolytic solution which contains a nitric acid again after this, for example. in that case as the electrolytic solution It is the solution which contains a nitric acid in 5-400g/l., and, as for the electrolysis processing time, it is [it is desirable that it is in the range of current density 1 - 200 A/dm2 and 30-80 degrees of solution temperature C, and] desirable that it is in the range for 5 - 90 seconds.
[0009] In this invention, the diameter of an electrolysis split-face-ized average pit of the 1st process is set to 2 micrometers - 25 micrometers. With making the diameter of an electrolysis split-face-ized average pit of a back process into 1/2 or less [of the diameter of an electrolysis split-face-ized average pit of a last process], and 1/30 or more In order to put a pit also on many [-fold] as a diameter of the 1st process electrolysis split-face-ized average pit which is specifically a last process 2-25 micrometers is desirable, water retention gets worse in less than 2 micrometers, and the difficulty of becoming dirty becomes poor in 25 micrometers or more. Since the pit formed at the 1st electrolysis split-face-ized process changes a lot at the 2nd electrolysis split-face-ized process and a water retention disposition top becomes impossible when it becomes 1/2 or more as a diameter of the 2nd process electrolysis split-face-ized average pit as a back process By less than 0.1 micrometers, 0.1-8 micrometers is desirable, and print durability changes, if larger than 8 micrometers, it will become dirty, and a sex gets worse. Especially 0.3-5 micrometers are desirable. Under the present circumstances, as etching processing, it is 0.01 - 20 g/m2. It is desirable and is 20 g/m2. If many, water retention will get worse, and it is 0.5 - 10 g/m2. It is especially desirable. Moreover, when performing electrolysis split-face-ization 3 times, as a diameter of an average pit of the formation of the 1st process electrolysis split face which is specifically a last process, 5-25 micrometers is desirable. By 25 micrometers or more, by less than 0.1 micrometers, water retention gets worse in less than 5 micrometers, and the difficulty of becoming dirty becomes poor, as a diameter of the 2nd process electrolysis split-face-ized average pit as a back process, 0.1-8 micrometers is desirable, and if larger than 8 micrometers, the difficulty of becoming dirty will get worse [print durability will get worse, and]. Especially 0.3-5 micrometers are desirable. As a diameter of the 3rd process electrolysis split-face-ized average pit, 0.1-2 micrometers is still more desirable, and especially 0.3-2 micrometers are desirable. As etching processing in that case, it is 0.01 - 20 g/m2 in the middle of the 1st and the 2nd process. It is desirable and is 0.5 - 10 g/m2. Although it is especially desirable, in middle etching processing of the 2nd process and the 3rd process, it is 0.01 - 8 g/m2. Although it is desirable, especially 0.3 - 5 g/m2 is desirable. In this invention, in order to make the diameter of an electrolysis split-face-ized average pit of a back process into 1/2 or less [of the diameter of an electrolysis split-face-ized average pit of a last process], and 1/30 or more, using the diameter of an electrolysis split-face-ized average pit of the 1st process as 2-25 micrometers, it is controllable by electrolytic-solution temperature, concentration, current density, the power line period, the power supply wave, FOADO, the current time ratio of reverse, etc. That is, the concentration which makes electrolytic-solution temperature of a back process higher than the electrolytic-solution temperature of a last

process makes a back process lower than a last process, current density makes a back process higher than a last process, a power line period makes a back process higher than a last process, and, therefore, the current ratio of forward reverse of a current wave form can control a back process easily rather than a last process to make a reverse current ratio high. Thus, the grain of the pit structure more than double which has the pit of the detailed and round shape of a uniform honeycomb in the pit side of a deep grain on the surface of an aluminum plate is generable.

[0010] Thus, the electrolysis-split-face--ization-processed aluminum plate is 0.01 - 8 g/m2 by chemical etching processing if needed in the solution which contains the acid or alkali of room temperature - 90 degreeC according to the method usually used. It is 0.3 - 5 g/m2 desirably. You may perform neutralization processing etc., after **********ing slightly. Slight etching may use the electrochemical technique, such as not only being immersed but electrolytic polishing. Furthermore, the outstanding base material for the printing versions can be obtained. Moreover, even if it carries out, it is not necessary to perform degreasing by the acid or alkali as pretreatment of the formation of an electrolysis split face performed as a conventional method, and washing processing. Like this invention, when not performing etching processing in middle, a grain configuration is complicated and a form is not ready, when after treatment is excluded, it becomes dirty, and a performance falls. By performing anodizing in the electrolytic solution which contains a sulfuric acid or a phosphoric acid according to the usual technique to the split-face board obtained as mentioned above, the base material for the printing versions excellent in a hydrophilic property, water retention, and print durability can be manufactured. Of course, after anodizing, it may be immersed into the solution containing sodium silicate etc., and hydrophilicity-ized processing may be performed.

[0011] Moreover, this invention is not restricted only to the aforementioned method, but after the formation of a mechanical split face, etching processing, and a desmut treatment, even if it repeats electrolysis split-face-ization and performs it, the same result is obtained. The surface roughness Ha of a bird clapper after the formation of a back process electrolysis split face is desirable 0.5 to 1.5 times to Ha after the formation of a last process electrolysis split face, and etching processing, and especially 0.8 to 1.2 times of this invention are desirable. Moreover, less than 80% and a bird clapper have a desirable rate of un-etching after each formation of an electrolysis split face, and especially less than 50% is desirable. The electrolysis method by this invention is applicable to both a batch process a half-continuous magnetization method and a continuous magnetization method. In this invention, as a desirable mode which manufactures the above-mentioned aluminum base material for the lithography versions As described above, to an aluminum plate before the formation of an electrolysis split face of the 1st process of the above The formation of a mechanical split face, 0.1-30/m2 Chemical etching processing is performed. electrolysis split-face-ization of this 1st process It is 50 - 600 c/dm2 in the electrolytic solution containing a 10-50-degree C nitric acid. It carries out. Before the formation of an electrolysis split face of a back process, it is 0.1 - 20 g/m2. Chemical etching processing is performed. It is 10 - 200 c/dm2 in the electrolytic solution which includes electrolysis split-face-ization of this back process for a 35-80-degree C nitric acid. It carries out and is 0.01 - 2 g/m2 after the formation of an electrolysis split face of a back process. Chemical etching processing, It is the manufacture method of the base material for the monotonous printing versions according to claim 1 characterized by performing anodizing. Although there is split-face-ization by an imprint, the brush, liquid honing, etc. as formation of a mechanical split face, split-face-izing with a brush is common. As split-face-izing with a brush, split-face-ization by the wire brush besides split-face-izing which a nylon brush depends can also be performed. In addition, print durability can be raised if mechanical split-face-ization is performed. the solution of an acid or alkali performs chemical etching processing performed after the formation of a mechanical split face -- having -- the amount of etching -- 0.1 - 30 g/m2 it is . The amount of etching is 0.1 g/m2. Dirt increases that it is the following and it is 30 g/m2. The difficulty of being involved deteriorates that it is above. especially -- desirable -- 5 - 15 g/m2 it is . Electrolysis split-face-ization of the 1st process is 50 - 600 c/dm2 in the 10-50-degree C nitric-acid electrolytic solution. It carries out. In this case, electrolytic-solution temperature deteriorates above 10 degrees C, and

the difficulty of being involved deteriorates above the increase of dirt, and 50 degrees C. It is 20-30 degrees C especially preferably. after the formation of an electrolysis split face of the 1st process -- again -- chemical etching processing -- the solution of an acid or alkali -- carrying out -- the amount of etching in this case -- 0.1 - 20 g/m2 it is . The amount of etching is 0.1 g/m2. Dirt is it increase and 20 g/m2 that it is the following. The difficulty of being involved deteriorates that it is above. especially -- desirable -- 5 - 15 g/m2 it is . Subsequently, it is electrolysis split-face-ization of a back process in the 35-80-degree C nitric-acid electrolytic solution 10 - 300 c/dm2 It carries out. Electrolytic-solution temperature deteriorates above 35 degrees C, and the difficulty of being involved deteriorates above the increase of dirt, and 80 degrees C. It is 40-70 degrees C especially preferably. after the formation of an electrolysis split face of a back process -- again -- chemical etching processing -- the solution of an acid or alkali -- carrying out -- the amount of etching in this case -- 0.01 - 2 g/m2 it is . The amount of etching is 0.01 g/m2. Dirt is it increase and 2 g/m2 that it is the following. The difficulty of being involved and print durability deteriorate that it is above. especially -- desirable -- 0.2 - 1.0 g/m2 it is . Anodic oxidation is given after the last chemical etching. Anodic oxidation passes current by using an aluminum base material as an anode plate in solution, such as a sulfuric acid, a phosphoric acid, a chromic acid, and oxalic acid, or a nonaqueous solution, and makes an anodic oxide film form in the front face of an aluminum base material. In addition, after performing each chemical etching processing at the above-mentioned process, it is desirable to perform the desmut treatment by the acid.

[0012]

[Example] Next, although an example explains this invention concretely, this invention is not limited only to this example.

(Example-1-3, example-of comparison1-2) The JIS1050-H16 aluminum rolled plate was immersed for 30 seconds by 50 degreeC into 5% caustic-alkali-of-sodium solution, and washing processing was performed. Then, they are 40degreeC-60degreeC and current density 40 A/dm2 to the inside of the solution which contains this aluminum plate a 15g [/l.] nitric acid after formation of mechanical split face, and chemical etching processing 15 g/m2, and a desmut treatment, each example, and the example of comparison, respectively. The diameter of an average pit was changed and electrolysis split-face-ized processing was carried out for 20 seconds. As a power supply wave, the square wave as shown in drawing 1 was used at that time. Next, after rinsing, in the liquid which contains 7% of aluminum concentration in caustic-alkali-of-sodium solution 25%, the portion equivalent to each edge of the pit which carried out being time immersed and which was generated by electrolysis split-face-ized processing was dissolved, and it rinsed. Next, it is current density 40 A/dm2 at the degree of considerable solution temperature which makes a 15g [/l.] nitric acid generate each diameter of the 2nd process average pit in the solution containing the aluminum concentration of 6g/l. again. Electrolytic etching was performed for 5 seconds. Thus, by making the aluminum hydroxide adhering to the front face of the obtained aluminum plate into a subject, it was immersed for 30 seconds into a 250g [/l.] sulfuric acid and solution of 50 degrees of solution temperature C, and the smut was removed and rinsed. Thus, the split-face board of the acquired examples 1-3 is 0.6 micrometers of average surface roughness, had uniform and precise double structural irregularity, and had the pit of the round shape of a small honeycomb on the big wave. Moreover, the amount of oxide films is 2.5 g/m2 to the aluminum plate obtained as mentioned above. Anodizing was performed in the solution which contains 100g /of sulfuric acids l. so that it may become. Thus, print durability was obtained in the difficulty of becoming dirty, and, as for the printing version obtained when the photosensitive layer was applied on the obtained aluminum plate and the printing version was manufactured, the good printing version was both obtained in the difficulty of being involved. Application-for-a-utility-model-patent conditions and a result are shown in Table 1.

[0013]

[Table 1]

表 1

例	電解粗面化第1工程平均ピット径		エッチング		電解粗面化第2工程平均ピット径		エッチング		印刷性能		
	μm	液温度℃	g/m²	秒	μm	液温度℃	g/m²	秒	汚れ難さ	耐刷性	絡み難さ
比較-1	2	40	1	20	-	-	-	-	△	○△	○△
実施-1	5	30	5	100	2	40	1	20	○	○	○
実施-2	15	20	5	100	2	40	1	20	○	○	○
実施-3	25	15	5	100	2	40	1	20	○△	○	◎○
比較-2	35	10	5	100	2	40	1	20	△×	○	◎

[0014] Washing processing is performed for an aluminum rolled plate in 5% caustic-alkali-of-sodium solution like the aforementioned example. (The example -3 of comparison, example-4-6) then, the inside of the solution which contains the aluminum concentration of 6g/l. for what carried out formation of mechanical split face, and chemical etching processing 15 g/m2, and the desmut treatment in a 15g [/l.] nitric acid -- 40degreeC and current density 40 A/dm2 After rinsing next, each sample set the diameter of an average pit of the 1st process to 15 micrometers, it was immersed into liquid of 7% of aluminum concentration in 25% caustic-alkali-of-sodium solution, and the portion equivalent to the edge of the pit generated by electrolysis split-face-ized processing was dissolved, and all rinsed. Next, it is current density 40 A/dm2 at the diameters 10 and 5 of the 2nd process average pit, and each degree of considerable solution temperature which generates 1 or 0.5 micrometers in the solution contained a 15g [/l.] nitric acid again, respectively. Electrolytic etching was performed for 5 seconds. Thus, it was immersed for 30 seconds into a 250g [/l.] sulfuric acid and solution of 50 degrees of solution temperature C, and the smut which made the subject the aluminum hydroxide adhering to the front face of the obtained aluminum plate was removed and rinsed. Thus, acquired example - To Ha after etching processing, the split-face board of 4-6 is 0.8 to 1.2 times, had uniform and precise double structural irregularity, and had the pit of the round shape of a small honeycomb on the big wave. Moreover, when the photosensitive layer was applied on the aluminum plate obtained as mentioned above and the printing version was manufactured, as for the obtained printing version, print durability and the good printing version of especially the difficulty of being involved were obtained in the difficulty of becoming dirty. Experiment conditions and a result are shown in Table 2.

[0015]

[Table 2]

表 2

例	電解粗面化第1工程平均ピット径		エッチング		電解粗面化第2工程平均ピット径		エッチング		印刷性能		
	μm	液温度℃	g/m²	浸漬時間	μm	液温度℃	g/m²	浸漬時間	汚れ難さ	耐刷	絡み難さ
比較-3	15	20	5	100	10	25	1	20	×	○	◎
実施-4	15	20	5	100	5	30	1	20	○△	○	◎○
実施-5	15	20	5	100	1	50	1	20	○	○	○
実施-6	15	20	5	100	0.5	60	1	20	◎○	○	○

[0016] (Example-7-10) The inside of the solution which contains a 15g [/l.] nitric acid after performing formation of mechanical split face, and chemical etching processing 15 g/m2, and a desmut treatment for a JIS1050-H16 aluminum rolled plate, and 40degreeC and current density 40 A/dm2 Electrolytic etching was performed for 20 seconds. As a power supply wave, the

square wave as shown in drawing 1 was used at that time. It was immersed in 90 degrees of solution C contained a 400g [/l.] after [rinsing] sulfuric acid for 120 seconds, and the portion equivalent to the edge of the pit generated by electrolysis split-face-ized processing was dissolved, and it rinsed. Next, inside of the solution contained a 15g [/l.] nitric acid again, and 40degreeC and current density 40 A/dm2 Electrolytic etching was performed for 5 seconds. The portion equivalent to the edge of the pit furthermore generated by electrolysis split-face-ized processing of the 2nd process was dissolved, and it rinsed. Next, the degree of solution temperature is changed, respectively to make each of diameters 3 and 2 of an electrolysis-among solution split-face-ized average pit which contain a 15g [/l.] nitric acid again, and 1 or 0.5 micrometers, and it is current density 40 A/dm2. Electrolytic etching was performed for 5 seconds. As after treatment after an electrolysis split-face-ized final process, they are chemical etching processing 1 g/m2 and ANODAIZU processing 2.5 g/m2. It carried out. Thus, acquired example - The rate of un-dirty after the formation of an electrolysis split face after etching processing is less than 50%, and had uniform and precise 3-fold structural ******, and the split-face liquid of 7-10 had the pit of the round shape of a small honeycomb on the big beat. Moreover, the photosensitive layer was applied on the aluminum plate obtained as mentioned above, and the printing version with which the printing version obtained when the printing version was manufactured was extremely excellent in print durability, especially the difficulty of being involved in the difficulty of becoming dirty was obtained. Experiment conditions and a result are shown in Table 3.

[0017]

[Table 3]

表 3

例	電解粗面化第1工程平均ピット径		エッチング		電解粗面化第2工程平均ピット径		エッチング		電解粗面化第3工程平均ピット径		印刷性能		
	μm	液温度℃	g/m²	浸漬時間	μm	液温度℃	g/m²	浸漬時間	μm	液温度℃	汚れ難さ	耐刷性	絡み難さ
実施-7	15	20	10	200	5	30	3	60	3	43	△	○	◎
実施-8	15	20	10	200	5	30	3	60	2	40	○△	○	◎
実施-9	15	20	10	200	5	30	3	60	1	50	○	○	◎○
実施-10	15	20	10	200	5	30	3	60	0.5	60	◎○	○	◎○

◎：優、 ○：良、 △：可、 ×：不良

[0018] The aluminum plate of JIS-1050 is used. (Example-11-20, example -4 of comparison) Mechanical split-face-ization is performed to JP,50-40047,B in rotational frequency 350rpm using the equipment of a publication. at 50 degrees C in 10% of caustic-alkali-of-sodium solution

Each chemical etching processing, The amount of anodic oxide films is 3.0 g/m2 in the 120g [/l.] sulfuric acid after carrying out on the processing conditions which show each electrolysis split-face-ization which used the electrolytic solution of 1% of nitric acids in Table 4 and performing DESUMATTO by the acid after the last chemical etching processing, and 45 degrees C of solution temperature. Anodizing was performed so that it might become. The photosensitive layer was applied on each obtained base material for the lithography versions, the lithography version was made, like the example-1 grade, the printing performance (it is [difficulty / of becoming dirty] print durability in the difficulty of being involved) was investigated, and the obtained result was shown in Table 4.

[0019]

[Table 4]

	処理条件						印刷性能		
	機械的粗面化	化学的エッチング	硝酸電解粗面化	化学的エッチング	硝酸電解粗面化	化学的エッチング	汚れ難さ	絡み難さ	耐刷性
比較例4	実施した	10 g/m²	50 ℃ 200c/dm²	2 g/m²	−	−	○	○	○
実施例11	実施した	10 g/m²	25 ℃ 400c/dm²	10 g/m²	60 ℃ 200c/dm²	1 g/m²	◎	◎○	◎○
12	〃	0.05	〃	〃	〃	〃	△	◎○	◎○
13	〃	35	〃	〃	〃	〃	◎	○△	◎○
14	〃	10	5 ℃ 400c/dm²	〃	〃	〃	○△	◎○	◎○
15	〃	〃	55 ℃ 400c/dm²	〃	〃	〃	◎	○△	◎○
16	〃	〃	25 ℃ 400c/dm²	0.05	〃	〃	○△	◎○	◎○
17	〃	〃	〃	25	〃	〃	◎	○△	◎○
18	〃	〃	〃	10	30 ℃ 200c/dm²	〃	○△	◎○	◎○
19	〃	〃	〃	〃	85 ℃ 200c/dm²	〃	◎	△	○
20	〃	〃	〃	〃	60 ℃ 200c/dm²	2.5	◎	○△	○

◎： 優　○： 良　△； 可

[0020]

[Effect of the Invention] In the manufacture method of the base material for the printing versions that this invention performs electrolysis split-face-ized processing in the middle repeatedly on both sides of etching processing of aluminum for an aluminum base material in the acid electrolytic solution By the manufacture method of the base material for the lithography versions characterized by making the diameter of an electrolysis split-face-ized average pit of a back process into 1/2 or less [of the diameter of an electrolysis split-face-ized average pit of a last process], and 1/30 or more, using the diameter of an electrolysis split-face-ized average pit of the 1st process as 2 micrometers - 25 micrometers By manufacturing what raised water retention much more and was superior to before, the outstanding thing which raised the performance much more in the difficulty of being involved was able to be manufactured. Moreover, in the manufacture method of the above-mentioned base material for the lithography versions, the base material for the lithography versions which has the further excellent property can be obtained by performing formation of a mechanical split face, and chemical etching processing before the formation of an electrolysis split face of the 1st process of the above, performing chemical etching processing after the formation of an electrolysis split face of a back

process the formation back of an electrolysis split face of the 1st process, and subsequently performing anodic oxidation. By manufacturing the lithography version from the aluminum split-face board created by this invention, especially the outstanding printing performance and the lithography version which does not have dirt nature with a performance in the difficulty of being involved can be made.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The power supply wave form chart of the square wave of the AC power supply concerning this invention
[Drawing 2] (c) a thing, which carried out phase-angle control of the AC-power-supply wave form chart concerning this invention, (a):sine wave, and the (b):sine wave by the thyristor: Square wave

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[Translation done.]

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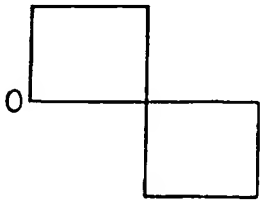
(54)【発明の名称】　平版印刷版用支持体の製造方法

(57)【要約】

【課題】　平版印刷版用支持体の製造方法において、従来より更に保水性を向上させることにより、絡み難さ性能を一段と向上させること。

【解決手段】　アルミニウム支持体を酸性電解液中で電解粗面化処理を、中間にアルミニウムのエッチング処理を挟んで繰り返しおこなう印刷版用支持体の製造方法において、第1工程の電解粗面化平均ピット径を２μｍ～２５μｍとして、後工程の電解粗面化平均ピッチ径を前工程の電解粗面化平均ピット径の1／2以下及至1／30以上にすることを特徴とする。その際電解粗面化処理用酸性電解液は、硝酸を主体とする水溶液であり、ピッチ径の変化は後工程の電解液温度，濃度，電流密度，電源周波数，電源波形，フォアード・リバースの電流時間比を前工程と異にすることによって制御出来る。



【特許請求の範囲】

【請求項1】 アルミニウム板を酸性電解液中で電解粗面化処理を、中間にアルミニウムのエッチング処理を挟んで繰返しおこなう印刷版用支持体の製造方法において、第1工程の電解粗面化平均ピット径を2μm～25μmとして、後工程の電解粗面化平均ピット径を前工程の電解粗面化平均ピット径の1／2以下乃至1／30以上にすることを特徴とする平版印刷版用支持体の製造方法。

【請求項2】 前記電解粗面化処理用酸性電解液が、硝酸を主体とする水溶液であることを特徴とする請求項1に記載の平板印刷版用支持体の製造方法。

【請求項3】 第1工程の電解粗面化の前に、アルミニウム板に機械的粗面化と、0．1～30／m^2の化学的エッチング処理を施し、該第1工程の電解粗面化を、10～50℃の、硝酸を含む電解液中にて50～600c／dm^2で行い、後工程の電解粗面化の前に、0．1～20g／m_2の化学的エッチング処理を施し、該後工程の電解粗面化を35～80℃の、硝酸を含む電解液中にて10～200c／dm^2で行い、後工程の電解粗面化の後に、0．01～2g／m^2の化学的エッチング処理と、陽極酸化処理を施すことを特徴とする請求項1に記載の平板印刷版用支持体の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、印刷版用支持体の製造方法に関するものであり、特にオフセット印刷版用に適する、粗面化されたアルミニウム板からなる印刷版用支持体の製造方法に関するものである。また、本発明は、絡み難さと汚れ難さに優れ、耐刷性にも優れた平版印刷版用支持体の製造方法にも関する。

【0002】

【従来の技術】印刷版用支持体、とくにオフセット印刷版用支持体としては、アルミニウム板（アルミニウム合金板を含む）が用いられている。一般にアルミニウム板をオフセット印刷用版材（支持体）として使用するためには、感光材との適度な接着性と保水性を有していることが必要である。この為にはアルミニウム板の表面を均一かつ緻密な砂目を有するように粗面化しなければならない。この粗面化処理は製版後実際にオフセット印刷を行ったときに版材の印刷性能や耐刷力に著しい影響を及ぼすので、その良否は版材製造上重要な要素となっている。印刷版用アルミニウム支持体の粗面化法としては交流電解エッチング法が一般に採用されており、電流としては普通の正弦波交流電流、矩形波などの特殊交番波形電流が用いられている。そして、黒鉛等の適当な電極を対極として交流電流により、アルミニウム板の粗面化処理を行うもので、通常一回の処理で行なわれている。そこで得られるピットの薄さは全体的に浅く、耐刷性能に劣るものであった。この為、その直径に比して深さの深いピットが均一かつ緻密に存在する砂目を有する印刷版用支持体として好適なアルミニウム板が得られるように、数々の方法が提案されている。その方法としては、交流を使った電解粗面化時の陽極時と陰極時の電気量の比率（特開昭54－65607号公報）、電源波形（特開昭55－25381号公報）、単位面積あたりの通電量の組み合わせ（特開昭56－29699号公報）などが知られている。また、機械的粗面化法と電解粗面化法を組み合わせた方法として特公昭57－16918号公報が知られている。更に又、アルミニウム支持体を酸性電解液中で電解粗面化処理を中間にアルミニウムのエッチング処理を挟んで繰返しおこなうことを特徴とする印刷版用アルミニウム支持体の製造方法（特公平7－29507号公報）が開示されている。

【0003】

【発明が解決しようとする課題】しかしながら、これらの方法は、汚れ性能と耐水性に優れた性能は示すものの、保水性を向上させることにより絡み難さ（網点部の非画像部の汚れ）性能を向上させることにおいては、不充分であった。

【0004】本発明の目的は、従来より更に保水性を向上させることにより、絡み難さ性能を一段と向上させることの出来る印刷版用支持体の製造方法を提供することにある。本発明の他の目的は、上記の絡み難さ性能の向上と共に、汚れ難さに優れ、かつ耐刷性にも優れた平版印刷版用支持体の製造方法を提供することにある。

【0005】

【課題を解決するための手段】本発明者等は、種々研究の結果、電化粗面化処理で生成したピットのエッジ部分の溶解処理をおこない、エッジ表面をなだらかにした後、ひきつづき再び硝酸を含む電解液中で交流電流波形を用いて前工程電解粗面化平均ピット径の1／2以下の後工程の電解粗面化平均ピット径を作製することによって、保水性を向上させ、絡み難さ性能を一段と向上させ得ることを発見し、本発明に至った。即ち、本発明の上記目的は、アルミニウム支持体を酸性電解液中で電解粗面化処理を、中間にアルミニウムのエッチング処理を挟んで繰返しおこなう印刷版用支持体の製造方法において、第1工程電解粗面化平均ピット径を2μm～25μmとして、後工程の電解粗面化平均ピット径を前工程の電解粗面化平均ピット径の1／2以下乃至1／30以上にすることを特徴とする平版印刷版用支持体の製造方法によって達成される。更に、上記の平版印刷版用支持体の製造方法において、好ましい態様としては、前記第1工程の電解粗面化の前に、アルミニウム板に機械的粗面化と、0．1～30／m^2の化学的エッチング処理を施し、該第1工程の電解粗面化を、10～50℃の、硝酸を含む電解液中にて50～600c／dm^2で行い、後工程の電解粗面化の前に、0．1～20g／m_2の化学的エッチング処理を施し、該後工程の電解粗面化を35

～80℃の、硝酸を含む電解液中にて10～200c/dm²で行い、後工程の電解粗面化の後に、0.01～2g/m²の化学的エッチング処理と、陽極酸化処理を施すことを特徴とする請求項1に記載の平板印刷版用支持体の製造方法である。

【0006】

【発明の実施の形態】本発明において、電解粗面化処理用酸性電解液は、硝酸を主体とする水溶液であることが好ましい。本発明において酸性電解液中で電解粗面化するということは、例えば硝酸を含む電解液中でアルミニウム板とこれに対向する電極との間に交流電流を流すことで、電解粗面化処理をおこなう。この場合、電解液としては硝酸を5～400g/リットルを含有する水溶液であり、電流密度1～200A/dm²、液温30～80°Cの範囲にあることが望ましい。電解粗面化処理時間は、5～90秒間の範囲にあることが好ましい。また、電解粗面化処理で使用する電流波形は交流に限定されるものではなく、直流電流を用いても可能である。本発明で用いる交流電流波形とは、正負の極性を交互に変換せしめて得られる波形の電流であって、図1及び図2にその電圧波形図を例示する。図2において、(a)は正弦波、(b)は正弦波をサイリスタで位相角制御したもの、(c)は矩形波の電源波形を示すが、本発明の交流波形は上記したものの電源波形に限るものではない。又本発明において電解粗面化処理に用いる電解液としては硝酸に限定されるものでなく、塩酸または塩酸と硝酸、硝酸と硫酸の混合液を用いてもよい。その際硫酸の代わりにリン酸もしくはリン酸と硫酸または他の酸との混合液を用いてもよい。

【0007】本発明において、電解粗面化処理の中間に挟むエッチング処理とは、前段の電解粗面化処理で生成したピットの特にエッジ部分の溶解を行なうことをいう。処理条件としては高温硫酸溶液への長時間浸漬によるアルミニウムのエッチングや、苛性ソーダへの浸漬、リン酸または硫酸電解液中での電解研磨など、周知のエッチング処理の手法がいづれも使用できる。ただし、電解粗面化処理後のエッチング液と電解粗面化処理液とが混合しないように、その前後で配慮する必要がある。

【0008】本発明において電解粗面化処理は、何回繰返しておこなってもよいが、中間でのエッチング処理を挟んで前一回、後1回とすることが、工程の簡素化上好ましい。本発明において電解粗面化処理をエッチング処理を挟んで繰返すということは、このあと再び例えば硝酸を含む電解液中でアルミニウム板とこれに対向する電極との間に交流電流を流す電解粗面化を行うことであり、その際電解液としては、硝酸を5～400g/リットルを含有する水溶液であり、電流密度1～200A/dm²，液温30～80°Cの範囲にあることが望ましく電解処理時間は5～90秒の範囲にあることが好ましい。

【0009】本発明において、第1工程の電解粗面化平均ピット径を2μm～25μmとして、後工程の電解粗面化平均ピット径を前工程の電解粗面化平均ピット径の1/2以下乃至1/30以上にすることとは、具体的には前工程である第1工程電解粗面化平均ピット径としては何重にもピットを重ねるためには、2～25μmが望ましく、2μm未満では保水性が悪化し、25μm以上では汚れ難さが不良となり、後工程としての第2工程電解粗面化平均ピット径としては1/2以上になると第1電解粗面化工程で形成されたピットが第2電解粗面化工程で大きく変化してしまい、保水性向上ができなくなるので、0.1～8μmが望ましく、0.1μm未満では耐刷性が変化し、8μmより大きいと汚れ性が悪化する。0.3～5μmが特に望ましい。この際エッチング処理としては、0.01～20g/m²が望ましく、20g/m²より多いと保水性が悪化し、0.5～10g/m²が特に望ましい。又、電解粗面化を3回行う場合、具体的には前工程である第1工程電解粗面化の平均ピット径としては5～25μmが望ましく、5μm未満では保水性が悪化し、25μm以上では汚れ難さが不良になり、後工程としての第2工程電解粗面化平均ピット径としては0.1～8μmが望ましく、0.1μm未満では耐刷性が悪化し、8μmより大きいと汚れ難さが悪化する。0.3～5μmが特に望ましい。更に第3工程電解粗面化平均ピット径としては0.1～2μmが望ましく、0.3～2μmが特に望ましい。その際のエッチング処理としては、第1と第2工程の中間には0.01～20g/m²が望ましく、0.5～10g/m²が特に望ましいが、第2工程と第3工程の中間のエッチング処理には0.01～8g/m²が望ましいが、0.3～5g/m²が特に望ましい。本発明において、第1工程の電解粗面化平均ピット径を2～25μmとして、後工程の電解粗面化平均ピット径を前工程の電解粗面化平均ピット径の1/2以下乃至1/30以上にするためには、電解液温度，濃度，電流密度，電源周波数，電源波形，フォアード，リバースの電流時間比等で制御可能である。即ち、後工程の電解液温度を前工程の電解液温度よりも高くする，濃度は後工程を前工程よりも低くし、電流密度は後工程を前工程より高くし、電源周波数は後工程を前工程よりも高くし、電流波形のフォワード・リバースの電流比は後工程を前工程よりもリバース電流比を高くすることに依って容易に制御し得る。このようにしてアルミニウム板の表面に深い砂目のピット面に微細で丸くかつ均一なハニカム状のピットを持つ2重以上のピット構造の砂目を生成することができる。

【0010】このようにして電解粗面化処理したアルミニウム板は、必要に応じ、通常用いられる方法に従って室温～90°Cの酸またはアルカリを含む水溶液中で化学エッチング処理により0.01～8g/m²に、望ましくは0.3～5g/m²に軽度にエッチングしたあ

と、中和処理などを施してもよい。軽度のエッチングは、浸漬のみならず、電解研磨などの電気化学的手法を用いてもよい。更に優れた印刷版用支持体を得ることができる。また、常法としておこなわれる、電解粗面化の前処理としての酸またはアルカリによる、脱脂、洗浄処理は、おこなっても、おこなわなくてもよい。本発明のように、中間でのエッチング処理を行なわないときには、砂目形状が複雑で形が整わず、後処理を省いたときに汚れ性能が低下する。以上のようにして得られた粗面板に対して通常の手法に従って硫酸またはリン酸を含む電解液中で陽極酸化処理をおこなうことにより、親水性、保水性、耐刷性ともに優れた印刷版用支持体を製造できる。もちろん陽極酸化処理後、ケイ酸ソーダなどを含む水溶液中に浸漬して親水化処理を行ってもよい。

【００１１】又、本発明は前記の方法だけに限られず、機械的粗面化，エッチング処理，デスマット処理後、電解粗面化を繰返し行っても、同様の結果が得られる。本発明は、後工程電解粗面化後の表面粗さHa が前工程電解粗面化，エッチング処理後のHa に対し、０．５～１．５倍になることが好ましく、０．８～１．２倍が特に望ましい。又、各電解粗面化後の未エッチング率が８０％未満となることが望ましく、５０％未満が特に望ましい。本発明による電解方法は、回分法、半連続法、連続法のいずれにも適用できる。本発明において、上記の平版印刷版用アルミニウム支持体を製造する好ましい態様としては、前記したように、前記第1 工程の電解粗面化の前に、アルミニウム板に機械的粗面化と、０．１～３０／m^2の化学的エッチング処理を施し、該第1 工程の電解粗面化を、１０～５０℃の、硝酸を含む電解液中にて５０～６００ｃ／ｄm^2で行い、後工程の電解粗面化の前に、０．１～２０ｇ／m^2の化学的エッチング処理を施し、該後工程の電解粗面化を３５～８０℃の、硝酸を含む電解液中にて１０～２００ｃ／ｄm^2で行い、後工程の電解粗面化の後に、０．０１～２ｇ／m^2の化学的エッチング処理と、陽極酸化処理を施すことを特徴とする請求項1 に記載の平板印刷版用支持体の製造方法である。機械的粗面化としては、転写、ブラシ、液体ホーニング等による粗面化があるが、ブラシによる粗面化が一般的である。ブラシによる粗面化としては、ナイロンブラシのよる粗面化の他、ワイヤーブラシによる粗面化も行うことができる。なお、機械的粗面化を行うと、耐刷性を向上させることができる。機械的粗面化の後に行う化学的エッチング処理は、酸またはアルカリの水溶液により行われ、エッチング量は、０．１～３０ｇ／m^2である。エッチング量が０．１ｇ／m^2以下であると、汚れが増加し、また３０ｇ／m^2以上であると絡み難さが劣化する。特に好ましくは、５～１５ｇ／m^2である。第1 工程の電解粗面化は、１０～５０℃の、硝酸電解液中にて、５０～６００ｃ／ｄm^2で行う。この場合、電解液温度が１０℃以上では汚れが増し、５０℃以上では、絡み難さが劣化する。特に好ましくは、２０～３０℃である。第1 工程の電解粗面化の後に、再度化学的エッチング処理を酸またはアルカリの水溶液で行い、この場合のエッチング量は、０．１～２０ｇ／m^2である。エッチング量が０．１ｇ／m^2以下であると、汚れが増し、また２０ｇ／m^2以上であると絡み難さが劣化する。特に好ましくは、５～１５ｇ／m^2である。次いで、後工程の電解粗面化を、３５～８０℃の、硝酸電解液中にて、１０～３００ｃ／ｄm^2で行う。電解液温度が３５℃以上では汚れが増し、８０℃以上では、絡み難さが劣化する。特に好ましくは、４０～７０℃である。後工程の電解粗面化の後に、再度化学的エッチング処理を酸またはアルカリの水溶液で行い、この場合のエッチング量は、０．０１～２ｇ／m^2である。エッチング量が０．０１ｇ／m^2以下であると、汚れが増し、また２ｇ／m^2以上であると絡み難さと耐刷性が劣化する。特に好ましくは、０．２～１．０ｇ／m^2である。最後の化学的エッチングの後で、陽極酸化を施す。陽極酸化は、硫酸、リン酸、クロム酸、しゅう酸、等の水溶液または非水溶液中でアルミニウム支持体を陽極として電流を流し、アルミニウム支持体の表面に陽極酸化皮膜を形成させる。なお、上記の工程で、各化学的エッチング処理を行った後には、酸によるデスマット処理を行うことが望ましい。

【００１２】

【実施例】次に実施例により本発明を具体的に説明するが、本発明はこの実施例のみに限定されるものではない。

（実施例－１～３，比較例－１～２）ＪＩＳ１０５０－Ｈ１６アルミニウム圧延板を５％苛性ソーダ水溶液中に５０°Ｃで３０秒間浸漬し、洗浄処理をおこなった。その後、機械的粗面化，化学エッチング処理１５ｇ／m^2、デスマット処理後に、このアルミニウム板を硝酸１５ｇ／リットル含有する水溶液中、各実施例及び比較例に対し夫々、４０°Ｃ～６０°Ｃ、電流密度４０Ａ／ｄm^2で平均ピット径を変えて２０秒間電解粗面化処理をした。その際電源波形としては、図1 に示すような矩形波を用いた。次に水洗後、２５％苛性ソーダ水溶液で、アルミニウム濃度7 %を含む液中に、それぞれの時間浸漬し、電解粗面化処理で生成したピットのエッジに相当する部分の溶解をおこない、水洗した。次に再び硝酸１５ｇ／リットルにアルミニウム濃度６ｇ／リットルを含有する水溶液中で、各第2 工程平均ピット径を発生させる相当液温度で、電流密度４０Ａ／ｄm^2で5 秒間電解エッチングを行った。このようにして得られたアルミニウム板の表面に付着した水酸化アルミニウムを主体としてスマットを硫酸２５０ｇ／リットル，液温５０°Ｃの水溶液中に３０秒間浸漬して除去し、水洗した。このようにして得られた実施例1 ～3 の粗面板は平均表面粗さ０．６μｍで、均一かつ緻密な2 重構造的凹凸をも

ち、大きなうねりの上に小さな丸いハニカム状のピットを有していた。また以上のようにして得られたアルミニウム板に酸化皮膜量が2．5g／m^2となるように硫酸を100g／リットル含有する水溶液中で陽極酸化処理を行った。このようにして得られたアルミニウム板上に感光層を塗布し、印刷版を製造したところ、得られた印刷版は汚れ難さ，耐刷性，特に絡み難さともに良好な印刷版が得られた。実験条件並びに結果を表1に示す。

【0013】

【表1】

例	電解粗面化第1工程平均ピット径		エッチング		電解粗面化第2工程平均ピット径		エッチング		印刷性能		
	μm	液温度℃	g/m^2	秒	μm	液温度℃	g/m^2	秒	汚れ難さ	耐刷性	絡み難さ
比較-1	2	40	1	20	-	-	-	-	△	○△	○△
実施-1	5	30	5	100	2	40	1	20	○	○	○
実施-2	15	20	5	100	2	40	1	20	○	○	○
実施-3	25	15	5	100	2	40	1	20	○△	○	◎○
比較-2	35	10	5	100	2	40	1	20	△×	○	◎

【0014】（比較例－3，実施例－4～6）前記例と同様にアルミニウム圧延板を5％苛性ソーダ水溶液中で洗浄処理をおこない、その後、機械的粗面化，化学エッチング処理15g／m^2、デスマット処理をしたものを、硝酸15g／リットル中にアルミニウム濃度6g／リットルを、含有する水溶液中に40°C，電流密度40A／dm^2で、第1工程の平均ピット径を各サンプル共に15μmにして、次に水洗後、いづれも25％苛性ソーダ水溶液中アルミニウム濃度7％の液中に浸漬して、電解粗面化処理で生成したピットのエッジに相当する部分の溶解を行い、水洗した。次に再び硝酸15g／リットル含有する水溶液中で、それぞれ第2工程平均ピット径10，5，1，0．5μmを発生させるそれぞれの相当液温度で電流密度40A／dm^2で5秒間電解エッチングを行なった。このようにして得られたアルミニウム板の表面に付着した水酸化アルミニウムを主体としたスマットを硫酸250g／リットル，液温50°Cの水溶液中に30秒間浸漬して除去し、水洗した。このようにして得られた実施例－4～6の粗面板はエッチング処理後のHaに対し、0．8～1．2倍であり、均一かつ緻密な2重構造的凹凸を持ち、大きなうねりの上に小さな丸いハニカム状のピットを有していた。また以上のようにして得られたアルミニウム板上に感光層を塗布し、印刷版を製造したところ、得られた印刷版は汚れ難さ，耐刷性，特に絡み難さの良好な印刷版が得られた。実験条件及び結果を表2に示す。

【0015】

【表2】

例	電解粗面化第1工程平均ピット径		エッチング		電解粗面化第2工程平均ピット径		エッチング		印刷性能		
	μm	液温度℃	g/m^2	浸漬時間	μm	液温度℃	g/m^2	浸漬時間	汚れ難さ	耐刷	絡み難さ
比較-3	15	20	5	100	10	25	1	20	×	○	◎
実施-4	15	20	5	100	5	30	1	20	○△	○	◎○
実施-5	15	20	5	100	1	50	1	20	○	○	○
実施-6	15	20	5	100	0.5	60	1	20	◎○	○	○

【0016】（実施例－7～10）JIS1050－H16アルミニウム圧延板を、機械的粗面化、化学エッチング処理15g／m^2，デスマット処理を行った後、硝酸15g／リットルを含有する水溶液中、40°C、電流密度40A／dm^2で20秒間電解エッチングをおこなった。その際電源波形としては、図1に示すような矩形波を用いた。水洗後硫酸400g／リットル含有する水溶液90°Cに120秒間浸漬し、電解粗面化処理で生成したピットのエッジに相当する部分の溶解を行い、水洗した。次に再び硝酸15g／リットル含有する水溶液中、40°C、電流密度40A／dm^2で5秒間電解エッチングをおこなった。更に第2工程の電解粗面化処理で生成したピットのエッジに相当する部分の溶解を行い、水洗した。次に再び硝酸15g／リットルを含有する水溶液中電解粗面化平均ピット径、それぞれ3，2，1，0．5μmを作るべくそれぞれ液温度を変え、電流密度40A／dm^2で5秒間電解エッチングを行った。電解粗面化最終工程後の後処理として、化学エッチング

処理1g／m^2、アノダイズ処理2．5g／m^2をおこなった。このようにして得られた実施例－7～10の粗面液はエッチング処理後の電解粗面化後の未エッチ率が50％未満であり、均一かつ緻密な3重構造的凹凸をもち、大きなうなりの上に小さな丸いハニカム状のピットを有していた。また以上のようにして得られたアルミニウム板上に感光層を塗布し、印刷版を製造したところ得られた印刷版は汚れ難さ、耐刷性、特に絡み難さが極めて優れた印刷版が得られた。実験条件及び結果を表3に示す。

【0017】

【表3】

例	電解粗面化第1工程平均ピット径		エッチング		電解粗面化第2工程平均ピット径		エッチング		電解粗面化第3工程平均ピット径		印刷性能		
	μm	液温度℃	g／m^2	浸漬時間	μm	液温度℃	g／m^2	浸漬時間	μm	液温度℃	汚れ難さ	耐刷性	絡み難さ
実施-7	15	20	10	200	5	30	3	60	3	43	△	○	◎
実施-8	15	20	10	200	5	30	3	60	2	40	○△	○	◎
実施-9	15	20	10	200	5	30	3	60	1	50	○	○	◎○
実施-10	15	20	10	200	5	30	3	60	0.5	60	◎○	○	◎○

◎：優、　○：良、　△：可、　×：不良

【0018】（実施例－11～20、比較例－4）JIS－1050のアルミニウム板を用い、特公昭50－40047号公報に記載の装置を用い、回転数350rpmにて機械的粗面化を行い、10％の苛性ソウダ水溶液にて、50℃にて各化学的エッチング処理と、硝酸1％の電解液を用いた各電解粗面化を表4に示す処理条件で行い、最後の化学的エッチング処理後に酸によるデスマットを行った後、硫酸120g／リットル、液温45℃にて、陽極酸化皮膜量が3．0g／m^2になるように陽極酸化処理を行った。得られた各平版印刷版用支持体上に感光層を塗布し、平版印刷版を作り、実施例－1等と同様に、印刷性能（汚れ難さ、絡み難さ、耐刷性）を調べ、得られた結果を表4に示した。

【0019】

【表4】

	処理条件						印刷性能		
	機械的粗面化	化学的エッチング	硝酸電解粗面化	化学的エッチング	硝酸電解粗面化	化学的エッチング	汚れ難さ	絡み難さ	耐刷性
比較例4	実施した	10 g/m²	50 ℃ 200c/dm²	2 g/m²	−	−	○	○	○
実施例11	実施した	10 g/m²	25 ℃ 400c/dm²	10 g/m²	60 ℃ 200c/dm²	1 g/m²	◎	◎○	◎○
12	〃	0.05	〃	〃	〃	〃	△	◎○	◎○
13	〃	35	〃	〃	〃	〃	◎	○△	◎○
14	〃	10	5 ℃ 400c/dm²	〃	〃	〃	○△	◎○	◎○
15	〃	〃	55 ℃ 400c/dm²	〃	〃	〃	◎	○△	◎○
16	〃	〃	25 ℃ 400c/dm²	0.05	〃	〃	○△	◎○	◎○
17	〃	〃	〃	25	〃	〃	◎	○△	◎○
18	〃	〃	〃	10	30 ℃ 200c/dm²	〃	○△	◎○	◎○
19	〃	〃	〃	〃	85 ℃ 200c/dm²	〃	◎	△	○
20	〃	〃	〃	〃	60 ℃ 200c/dm²	2.5	◎	○△	○

◎：優　○：良　△：可

【００２０】

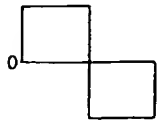
【発明の効果】本発明は、アルミニウム支持体を酸性電解液中で電解粗面化処理を中間にアルミニウムのエッチング処理を挟んで繰り返しおこなう印刷版用支持体の製造方法において、第1工程の電解粗面化平均ピット径を2μm～25μmとして、後工程の電解粗面化平均ピット径を前工程の電解粗面化平均ピット径の1／2以下乃至1／30以上にすることを特徴とする平版印刷版用支持体の製造方法によって、従来より一段と保水性を向上させ優れたものを製造することにより、絡み難さ性能を一段と向上させた優れたものを製造することが出来た。また、上記の平版印刷版用支持体の製造方法において、前記第1工程の電解粗面化の前に機械的粗面化と化学的エッチング処理を行い、第1工程の電解粗面化の後と、後工程の電解粗面化の後に化学的エッチング処理を行い、次いで陽極酸化を行うことによって、更に優れた特性を有する平版印刷版用支持体を得ることができる。本発明によって作成されたアルミニウム粗面板から平版印刷版を製造することにより、優れた印刷性能と特に絡み難さ性能をもちかつ汚れ性のない平版印刷版を作ることが出来る。

【図面の簡単な説明】

【図1】本発明に係わる交流電源の矩形波の電源波形図

【図2】本発明に係わる交流電源波形図、（ａ）：正弦波、（ｂ）：正弦波をサイリスタで位相角制御したもの、（ｃ）：矩形波

【図1】



【図2】